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PROPERTIES OF NONAQUEOUS ELECTROLYTES

SECOND QUARTERLY REPORT

(20 September 1966 to 19 December 1966)

By
Rudolf Keller
James N. Foster
James D. Ray
Jack M. Sullivan

Prepared For

National Aeronautics and Space Administration

Contract NAS3-8521

Rocketdyne
A Division of North American Aviation, Inc.
Canoga Park, California

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Rocketdyne
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FOREWORD

This report was prepared under G.O. 8852 in compliance with Article VI and Paragraph B of Contract NAS3-8521 for the National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio. The work was conducted in the Chemistry Section of Rocketdyne's Research Division, during the period 20 September through 19 December 1966.

ABSTRACT

A complete vapor phase chromatographic analysis of dimethyl formamide was conducted, and several techniques were utilized to verify the water content of propylene carbonate and dimethyl formamide. Solutes were characterized by spark source mass spectrometry and emission spectroscopy.

Physical properties such as the density, viscosity, and conductance of electrolytes containing LiCl and/or $AlCl_3$ in dimethyl formamide were determined.

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SUMMARY

Propylene carbonate, dimethyl formamide, and acetonitrile were distilled during the report period. Dimethyl formamide was completely characterized by vapor phase chromatography. Several methods [vapor phase chromatography (VPC), nuclear magnetic resonance (NMR), and Karl Fischer titration] were utilized to verify the water content of distilled propylene carbonate.

Some solutes were analyzed by spark source mass spectrometry and emission spectroscopy. Because no crucial inpurities at levels of 100 ppm or more were revealed, it was decided to utilize the chemicals, i.e., lithium chloride, aluminum chloride, lithium fluoride, tetramethylammonium hexafluorophosphate, and cupric chloride, without any further purification.

Physical properties such as density, viscosity, and conductance were determined for LiCl/DMF, $AlCl_3$/DMF, and LiCl-$AlCl_3$/DMF solutions. The solubilities of LiCl and $AlCl_3$ in dimethyl formamide were determined.

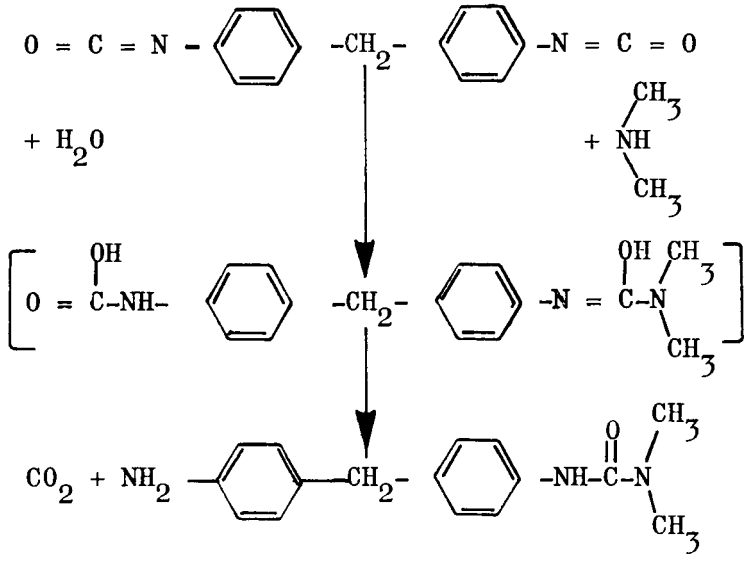
DESCRIPTION OF PROGRESS

PREPARATION OF ELECTROLYTES

Purification of Solvents

Propylene carbonate was distilled as described in Ref. 1.

Spectrograde dimethyl formamide (99.9-percent purity) was distilled at a pressure of 25 mm Hg using a Vigreux column. Dimethyl formamide was distilled from Multrathane M (Mobay Chemical Company) to reduce the content of water and amines. A schematic representation of the reaction of Multrathane M (p, p' diphenylmethane diisocyanate) with water and dimethlamine is as follows:



From gas chromatographic data, it was determined that the water content was reduced from 230 to 50 ppm (by weight). Furthermore, the lower boiling impurities were reduced to a great extent. Neither predistillation

from CaH_2 nor an additional distillation through a 30-plate Oldershaw column produced significantly different results. This indicated that dimethyl formamide of acceptable purity may be obtained by a relatively simple purification procedure and approximately 2 liters have been so obtained.

Approximately 1 liter of spectrograde acetonitrile was purified by double distillation from P_2O_5 on the spinning band colum. Karl Fisher titration analysis of this material indicated a water content of 23 ppm. A 2-1/2-foot, 1-inch-diameter, electrically heated Heli-pak packed column is being assembled for future use as an alternative to the spinning band column.

Analysis of Solvents by Vapor Phase Chromatography

Dimethyl Formamide. The procedure for a complete VPC analysis of dimethyl formamide has been finalized; one batch of purified dimethyl formamide, was analyzed on three columns. One column was packed with Porapak Q; this column is used primarily for the determination of water. The remaining two columns were packed with Apiezon L and Carbowax 20M on Chromosorb. These two columns are used for the determination of organic matter.

The procedure for the determination of water was described in the Ref. 1. The eluent from the Porapak Q column is monitored with a cross-section detector. The response for water in dimethyl formamide was determined to be 67 ppm/cm^2 by adding known amounts of water to the dimethyl formamide and measuring the resulting area of the water peak. The response determined for various water concentrations in dimethyl formamide is presented in Table 1. The response determined by the same procedure (Fig. 4)* for

*Figure 4 is presented on page 12.

water in propylene carbonate was 50 ppm/cm^2. These values are different because the water concentrations are reported on a weight basis. Thus, the 100-microliter samples correspond to 94 milligrams of dimethyl formamide and 120 milligrams of propylene carbonate. The responses for water in dimethyl formamide and propylene carbonate are in agreement within the experimental accuracy of the method, if they are expressed on a volume basis, i.e., the responses are 64 and 60 ppm/cm^2 (parts per million by volume), respectively.

TABLE 1

RESPONSE OF CROSS-SECTION DETECTOR TO VARIOUS AMOUNTS OF WATER IN DIMETHYL FORMAMIDE

Sample No.	H_2O, ppm	H_2O Peak Area, cm^2
1	X*	1.7
2	X + 106	3.6
3	X + 252	5.4

*The sample to which the water was added contained an unknown amount of water, X. Based on the response of 67 ppm/cm^2, X is 110 ppm.

To verify the results determined by the VPC technique, a sample of dimethyl formamide was analyzed by the Karl Fischer method. The water content determined by VPC and Karl Fischer methods was 93 and 83 ppm, respectively. These values are in agreement within the experimental accuracy of the two methods.

Figure 1 shows chromatograms for two samples of dimethyl formamide, an undistilled and a distilled sample of spectroquality material (designated DMF #4 and DMF #4-1, respectively). In each chromatogram, the first and second peaks are air (oxygen and/or nitrogen) and carbon dioxide; the third peak is water. The undistilled product contained 230 ppm water and the distilled material contained 50 ppm water.

The cross-section detector indicated approximately the same response for formic acid, formaldehyde, water, and methanol. Formic acid, formaldehyde, and methanol were eluted after water and before dimethyl formamide. Because no peaks were found on the chromatogram for the distilled dimethyl formamide between the water peak and the dimethyl formamide peak, the concentration of formic acid, formaldehyde, and methanol each was less than 10 ppm.

Vapor phase chromatographic analysis utilizing a single column is not definitive because an impurity could be eluted at the same time as the major component or an impurity could have a very long retention time. Relatively long retention times appear to be characteristic of Porapak columns. Dimethyl formamide, for example, has a retention time of 8 minutes at 200 C on Porapak Q, but is not retained on Carbowax 20M or Apiezon L at this temperature. Changing the nature of the column, particularly the polarity of the liquid phase, results in a change of the retention times for each component. Thus, two components that have the same retention time on a nonpolar column (because of the similarity in their boiling points) may have different retention times on a polar column (because of the difference in their polarities).

Dimethyl formamide was analyzed on polar and nonpolar columns. The polar column was 5 percent Carbowax 20M on Chromosorb W (DMCS-AW, 60/80 mesh) packed in 1/8-inch by 20-foot stainless-steel tubing. The nonpolar column was packed with 5 percent Apiezon L on Chromosorb W (DMCS-AW, 60/80

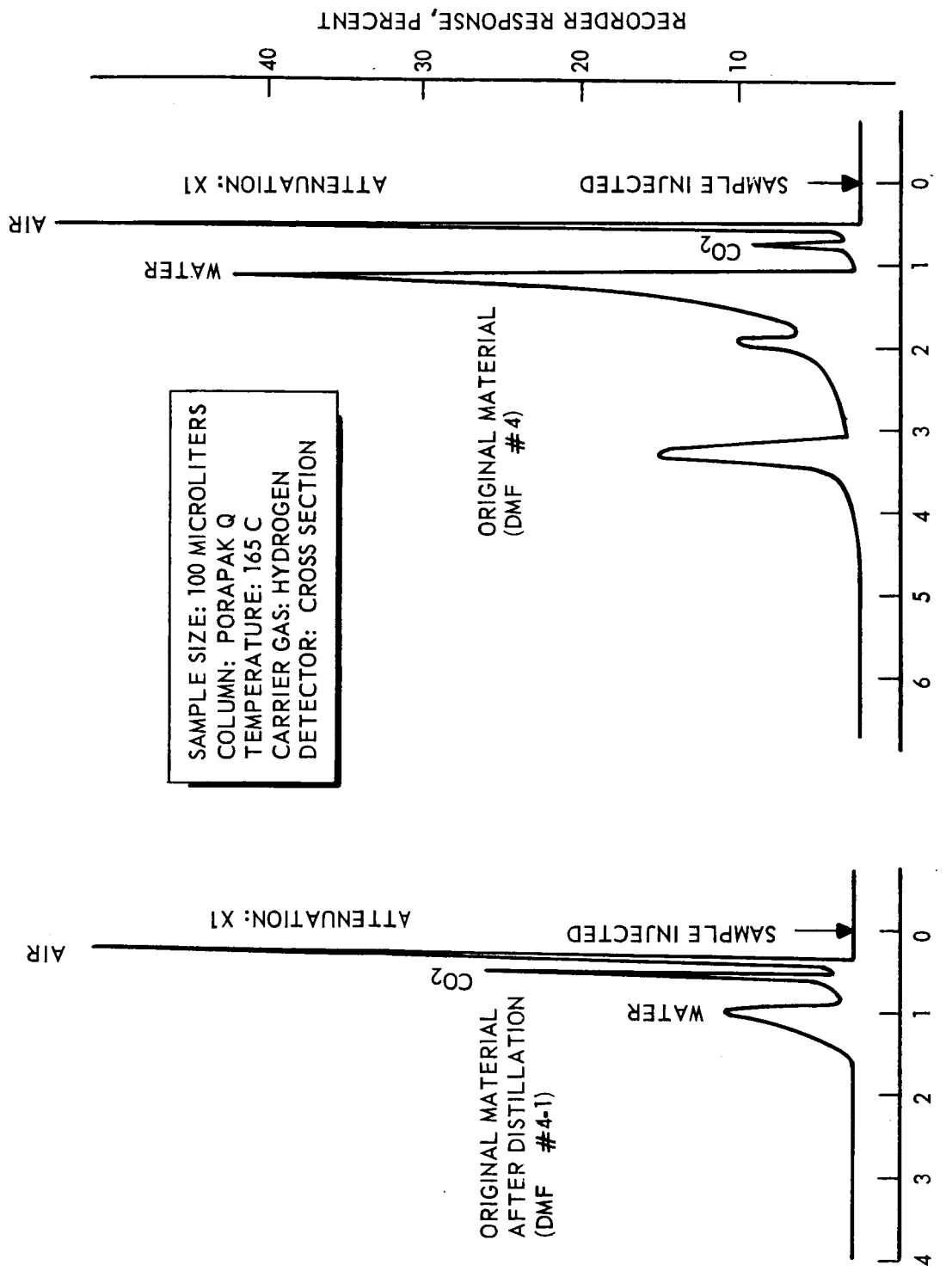


Figure 1. Initial Portion of Chromatograms of Spectroquality Dimethyl Formamide

mesh);this was packed in 1/8-inch by 10-foot stainless-steel tubing. A flame-ionization detector was employed with these two columns. Several chromatograms were made at different temperatures to obtain sharp, easily delineated peaks. For peaks which appear ahead of dimethyl formamide, better resolution is generally obtained at lower temperatures; peaks which follow the dimethyl formamide peak are generally sharper at higher temperatures. Programmed temperature gas chromatography usually results in good resolution and peak shape because of the increasing temperature during elution of the sample. Because of the upper limit placed on impurities (100 ppm), several isothermal chromatograms obtained at different column temperatures are more preferable than one gas chromatogram with programmed temperature control. This is because there is better stability and reproducibility inherent in the isothermal technique.

Chromatograms were obtained for a batch of distilled dimethyl formamide, DMF#4-1, on the Carbowax 20M column at temperatures of 66, 96, and 165 C. Figure 2 shows a chromatogram of DMF#4-1 on Carbowax 20M at 96 C. In general, all of the chromatograms were similar. Two peaks appeared at the beginning of the chromatograms at 96 and 165 C followed by a peak for dimethyl formamide. There were no peaks observed after that of dimethyl formamide even though the chromatogram was continued for 40 minutes after the elution of dimethyl formamide.

Chromatograms were also obtained for DMF#4-1 on an Apiezon L column at temperatures of 40, 102, and 165 C. Figure 3 shows a chromatogram on Apiezon L at 102 C. Two peaks which were not well resolved appeared at the beginning of the chromatograms at 102 and 165 C, followed by a peak for dimethyl formamide. Neither an Apiezon L column nor a Carbowax 20M column produced peaks after that of dimethyl formamide.

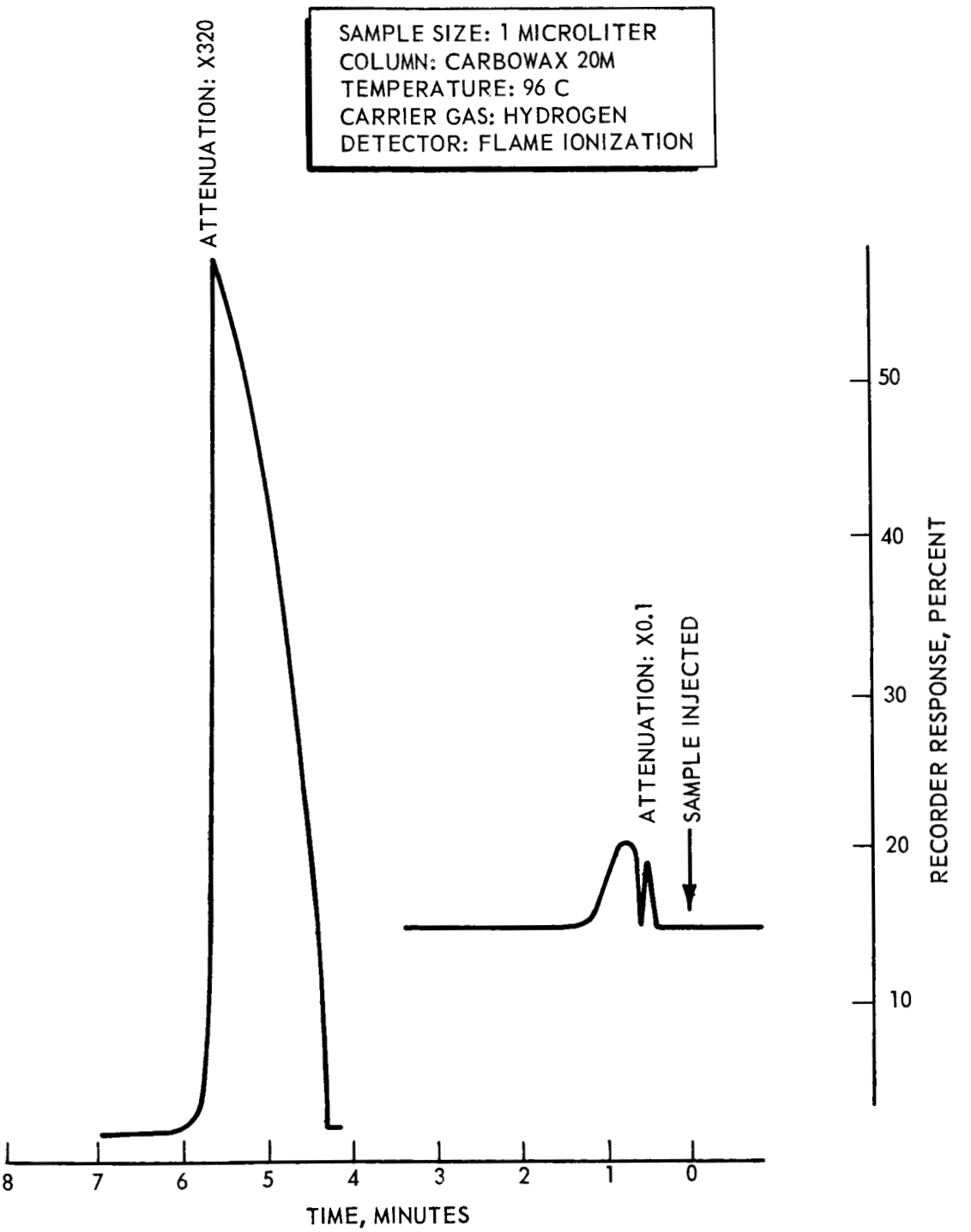


Figure 2. Chromatogram of Distilled Spectroquality Dimethyl Formamide, DMF #4-1, on Carbowax 20M

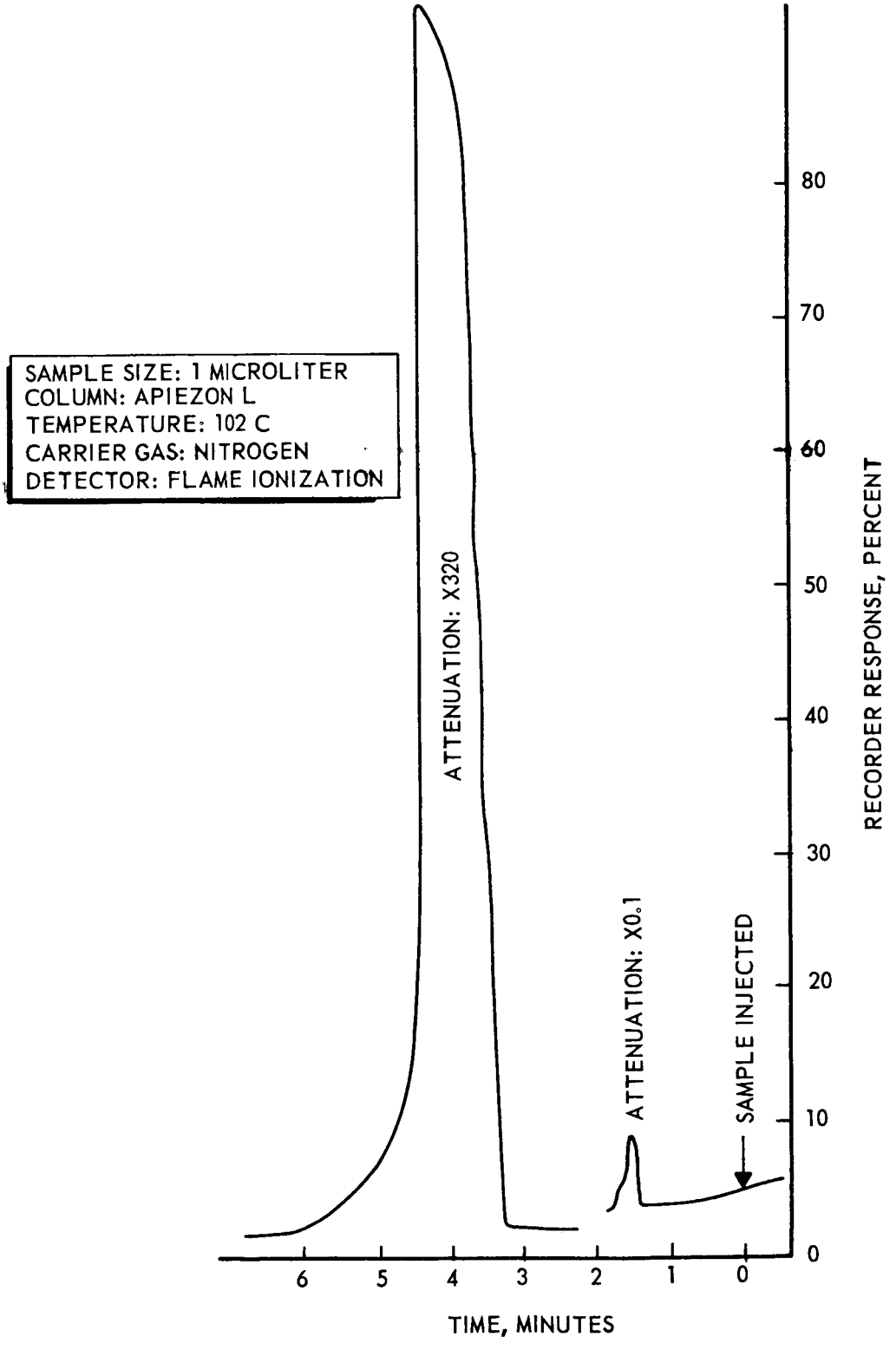


Figure 3. Chromatogram of Distilled Spectroquality Dimethyl Formamide, DMF #4-1, on Apiezon L

The area of the dimethyl formamide peak corresponds to 6000 cm^2. For most organic compounds, the area of the response of the flame-ionization detector is proportional to the weight of compounds being analyzed. As a result, if an organic impurity is present with a concentration of 100 ppm, a peak with an area of 0.6 cm^2 would be expected. On the most sensitive range, the area of the response would be 6 cm^2 which corresponds to a triangular peak with a base of 1 centimeter and a height of 12 centimeters. No such peaks were found on either column.

The analytical results on the Porapak Q column with a cross-section detector were compared with those obtained on Carbowax 20M and Apiezon L columns with the flame-ionization detector. It was concluded that no impurity is present in the distilled spectroquality dimethyl formamide, DMF#4-1, with a concentration greater than 100 ppm.

Propylene Carbonate. Complete characterization of propylene carbonate was not accomplished but uncertainties in the water determination have been resolved.

When propylene carbonate was first analyzed, water concentrations were much higher than reported by other workers who distilled propylene carbonate. Furthermore, water appeared as two peaks rather than one peak. Figure 4 shows the initial portion of chromatograms of propylene carbonate containing various amounts of water. From this, a response of 50 ppm/cm^2 was determined. The reliability of the water determination in propylene carbonate was substantiated by the following facts:

1. The capability of the method to determine low water contents was demonstrated by an analysis of propylene carbonate which had been dried with Linde Molecular Sieve 4A; this sample contained 20 ppm water.

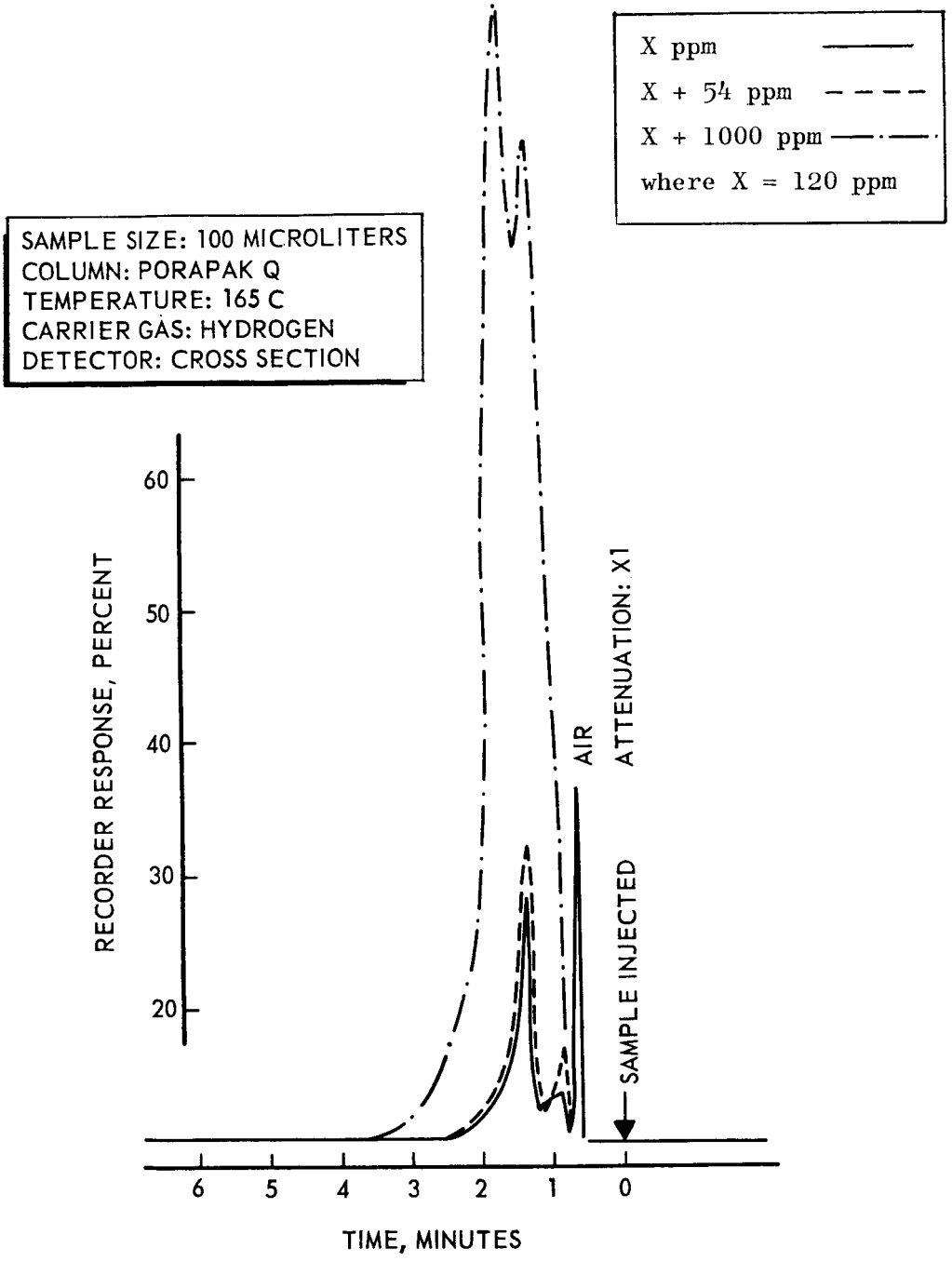


Figure 4. Chromatograms of Propylene Carbonate Containing Various Amounts of Water

2. The addition of aliquots of water to a sample of propylene carbonate increased the size of both chromatographic peaks.

3. The response factor for water in propylene carbonate (using the area of both peaks) is essentially the same as the response factor for water in dimethyl formamide.

4. The Karl Fischer method results agree with those found by the VPC method. The Karl Fischer method indicated that there were 158 ppm water in a sample which analyzed as 180 ppm by VPC.

5. The water content obtained by the NMR method is identical with that obtained by the VPC method (200 ppm for a particular sample).

Analysis of Solvents by Karl Fischer Titration

As an independent check of the results obtained by VPC, Karl Fischer reagent (Ref. 2) has been employed to determine water content. To date, Karl Fischer titration is the only method utilized to determine the water content in acetonitrile.

Karl Fischer reagent is a well specified mixture of pyridine, iodine, methanol, and sulfur dioxide. The titration of H_2O in this CH_3OH solution involves a sequence of reactions that can be represented by the following equations:

$$C_5H_5N.I_2 + C_5H_5N.SO_2 + C_5H_5N + H_2O \longrightarrow 2\ C_5H_5N.HI + C_5H_5N{-}SO_2 \quad (O)$$

and

$$C_5H_5N{-}SO_2 \quad (O) + CH_3OH \longrightarrow C_5H_5N.HSO_4CH_3$$

The standard reagent titrates 5 milligrams of water per milliliter of titrant. To determine trace quantities of water in solvents, the titrant was diluted with methanol to an activity of ~1 mg H_2O/ml titrant. If 100 grams (~100 milliliters) of solvent are titrated, each milliliter of titrant corresponds to 10 ppm of water, giving a 1 milliliter titration with a 5-milliliter micro-burette (0.01 ml/div). The lower limit for the determination of water is less than 10 ppm. The direct titration endpoint was determined potentiometrically and the titrations were performed in a closed system. The titrant was standardized against the water of hydration of weighed quantities of sodium tartrate.

Several substances interfere with Karl Fischer analyses including: alkaline materials, compounds containing active hydrogen, and strong oxidizing or reducing agents. One problem associated with large sample sizes is the disruption of the electrolytic nature of the titration system such that the standard endpoint cannot be employed. This problem was not found in the titration of propylene carbonate or acetonitrile.

The titration of dimethyl formamide containing small amounts of water was unusual because the endpoint was passed when the first drop of Karl Fischer reagent was added. This was because the reagent slowly reacted with the sample; subsequent additions of reagent reacted rapidly so that the sample could be titrated in the usual fashion. This reaction appears to be autocatalytic, but the mechanism was not investigated.

Analysis of Solvents by Nuclear Magnetic Resonance

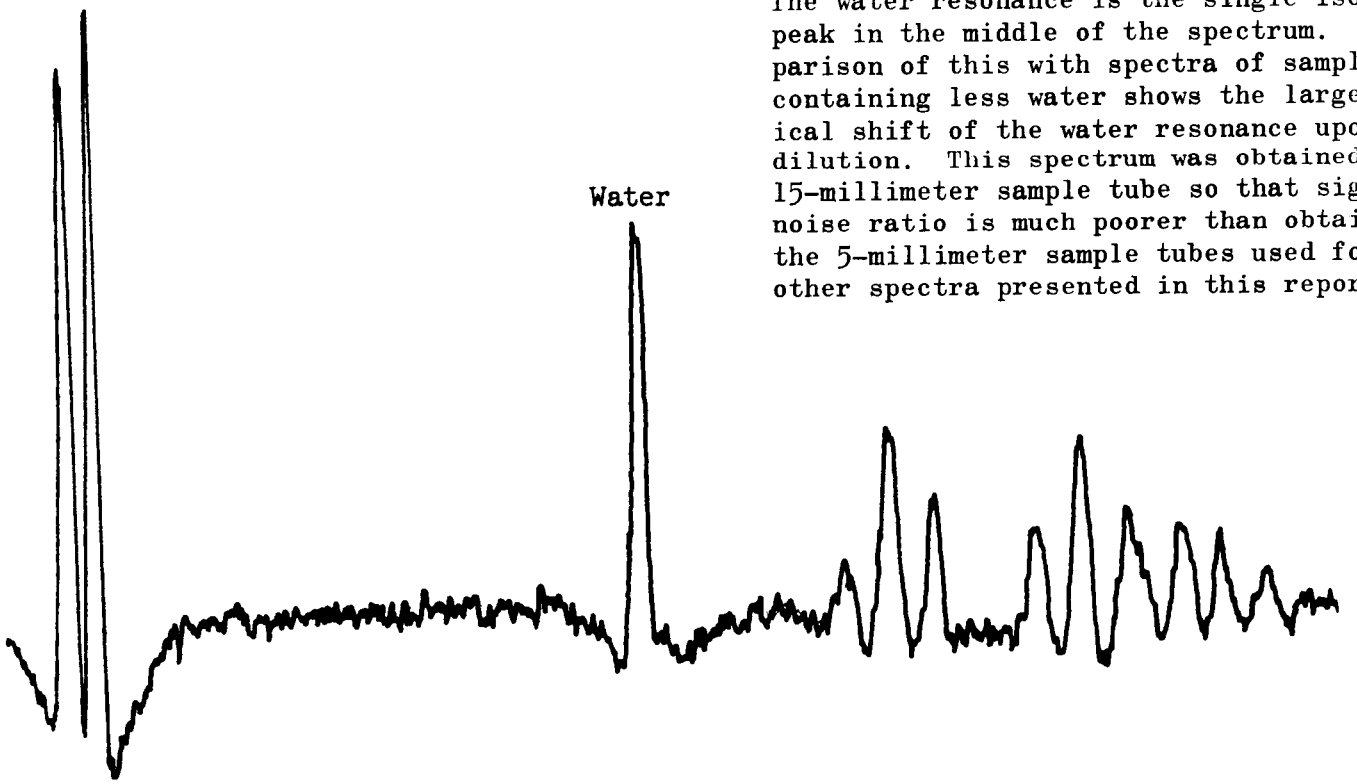
The immediate objective of the present NMR studies was to obtain an independent analysis for impurities in the solvents. In particular, a method in addition to VPC and Karl Fischer titration to analyze for water was

desirable. The measurements taken are not only valuable in regard to the analytical aspects of the program but also constitute the necessary basis for the structural NMR studies.

The NMR technique employed was developed under another contract (Ref. 3). Previous experience acquired at Rocketdyne on the analysis of water in nitrogen tetroxide had revealed that the detection limit for water was 50 ppm. Because some acetonitrile samples were analyzed as less than this, it was desriable to improve the NMR sensitivity. The use of broad-line techniques, with a modulating field of 1.5 Hz and an amplitude in gauss comparable to the natural line widths observed in proton spectra produced the desired improvement in sensitivity. At present, as judged by the spectra presented in this report, the sensitivity is approximately 1 ppm when scan rates of some 100 Hz per hour are used.

All the spectra presented in Fig. 5 through 9 were obtained by use of a Varian Associates high-resolution 60 MHz radio-frequency unit, high-resolution magnet equipped with flux stabilizer and field homogeneity controls, and a Princeton Applied Research lock-in-amplifier. The spectra are therefore all displayed as the second derivative of the absorption mode.

Figure 5 displays the sprectrum of propylene carbonate containing 10 percent water, utilizing a 15-millimeter sample tube. The signal-to-noise ratio is not as good as that obtained by the use of 5-millimeter sample tubes which were used for all of the other spectra. The spectrum is included for future reference in interpreting chemical shifts of water as a function of dilution. For this comparison, Fig. 6 through 8 show the spectra of propylene carbonate to which 8500 and 930 ppm water had been added to a sample that was analyzed as 200 ppm water by VPC.



The water resonance is the single isolated peak in the middle of the spectrum. Comparison of this with spectra of samples containing less water shows the large chemical shift of the water resonance upon dilution. This spectrum was obtained in a 15-millimeter sample tube so that signal-to-noise ratio is much poorer than obtained with the 5-millimeter sample tubes used for all other spectra presented in this report.

Figure 5. Proton NMR Spectrum of Propylene Carbonate Containing 10 Percent H_2O

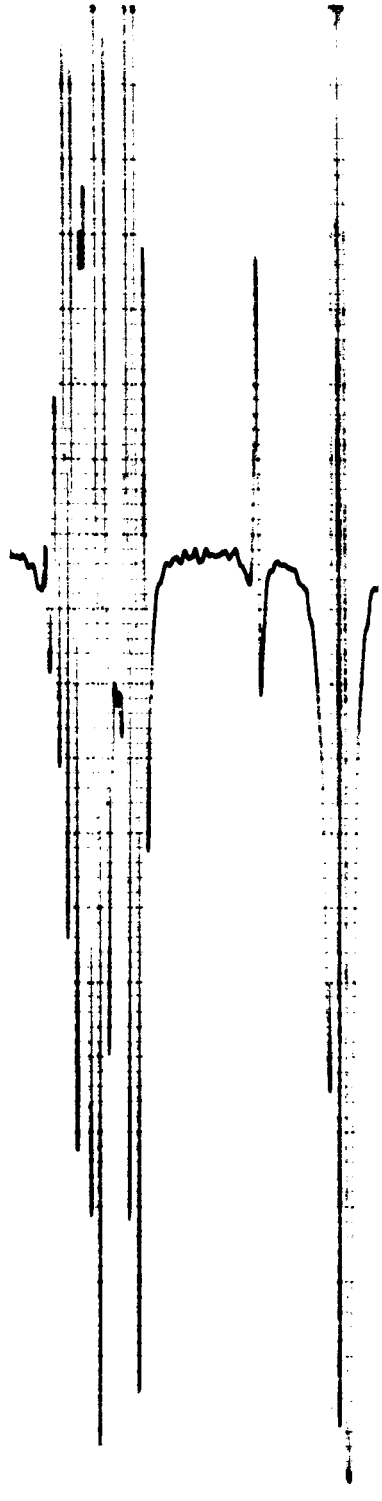


Figure 6. Proton Spectrum of Propylene Carbonate Containing 0.85-Percent Added H_2O; Second Derivative Display (The water line is the singlet in the middle of the spectrum)

This H^1 spectrum at 60 MHz has sufficient gain to show the carbon 13 sidebands and in addition shows the presence of 1130-ppm water. The large second derivative doublet on the right which is due to the methyl group is flanked on either side by small doublets caused by carbon 13 splitting of the methyl resonance. The water resonance is just at the right of the left pair of carbon 13 sidebands.

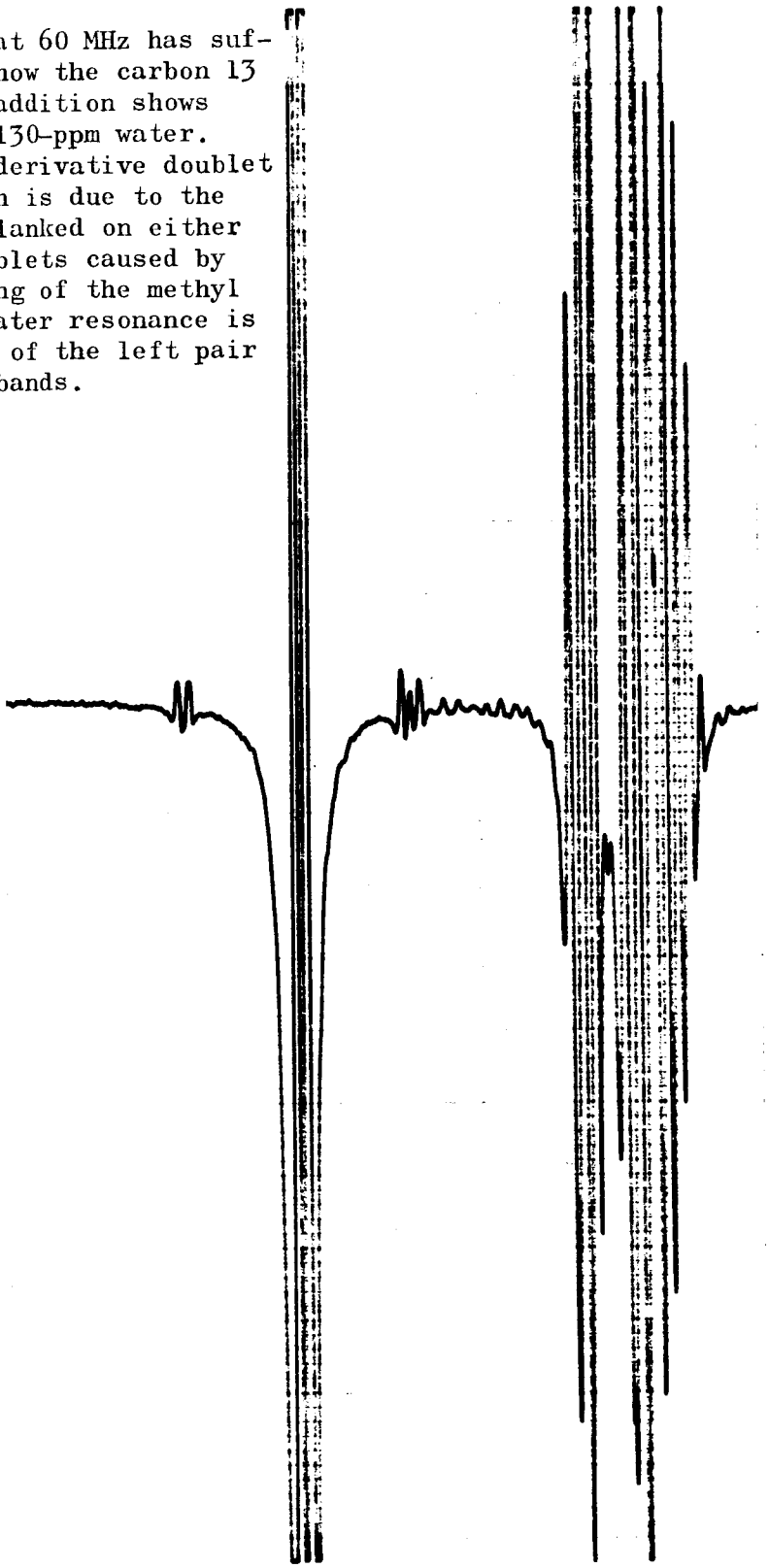


Figure 7. High Resolution Spectrum of Propylene Carbonate Obtained by Using 1.5 Hz Lock-In-Amplifier Detection

The water resonances are on the left. Spectrum on right is a sample of propylene carbonate containing 200 ppm H_2O (by VPC) to which 0.093 percent H_2O was added. (Second derivative display of H^1 resonances at 60 MHz.)

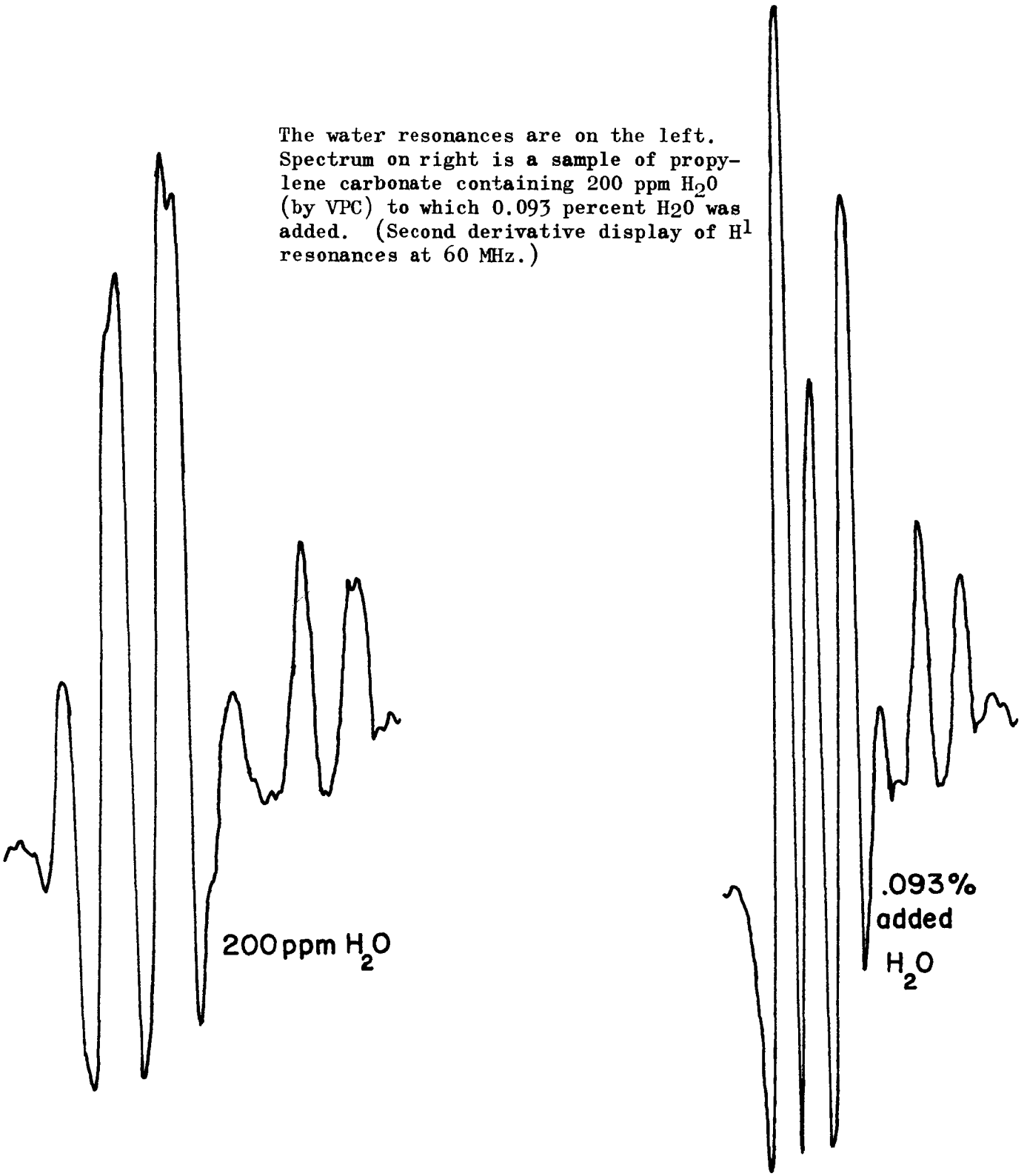


Figure 8. High Gain Display of Carbon 13 Sidebands and Water Resonances in Propylene Carbonate

The top of the usual absorption mode would be at the bottom of the figure in each case; differentiation inverts this. Figure 5 appears more nearly like an ordinary high-resolution absorption mode spectrum; however, the wings extending below the base line on each side of a line are quite evident. With the higher resolution afforded by the smaller size sample tubes and sample spinning, these wings become extremely large in Fig. 6 through 8. None of the spectra are well phased so as to produce perfectly symmetrical peaks and wings; however, the phasing is nearly perfect in Fig. 5 and 7.

Figure 8 displays spectra used in the analysis of water content of propylene carbonate. The spectrum on the left was of a sample containing 200 ppm water which had been analyzed by VPC. The spectrum on the right is of the same propylene carbonate batch to which 0.093 percent water had been added. For evaluation of the actual concentration in the 200 ppm sample, the following equation was used:

$$\frac{X \text{ ppm} + 930 \text{ ppm}}{X \text{ ppm}} = \frac{340}{100} \cdot \frac{8}{5}$$

Here, 340/100 is the ratio of the combined areas of the two peaks referred to the total areas of the peaks above a line drawn between the two peak wing minima. The ratio 8/5 refers to the distance between the peaks in the two spectra (the scan rates were not identical). The value for water concentration (X) deduced in this way is 200 ±20 ppm, in agreement with that found by VPC. Both precision and sensitivity could be increased by slower scan speed and higher gain, respectively.

In addition to constituting an analysis for water, the NMR study has shown the absence of any other organic impurities in propylene carbonate in amounts greater than 10 ppm. This conclusion is based on the fact that spectra were run over the entire range of known proton resonances without detecting resonances other than those of propylene carbonate.

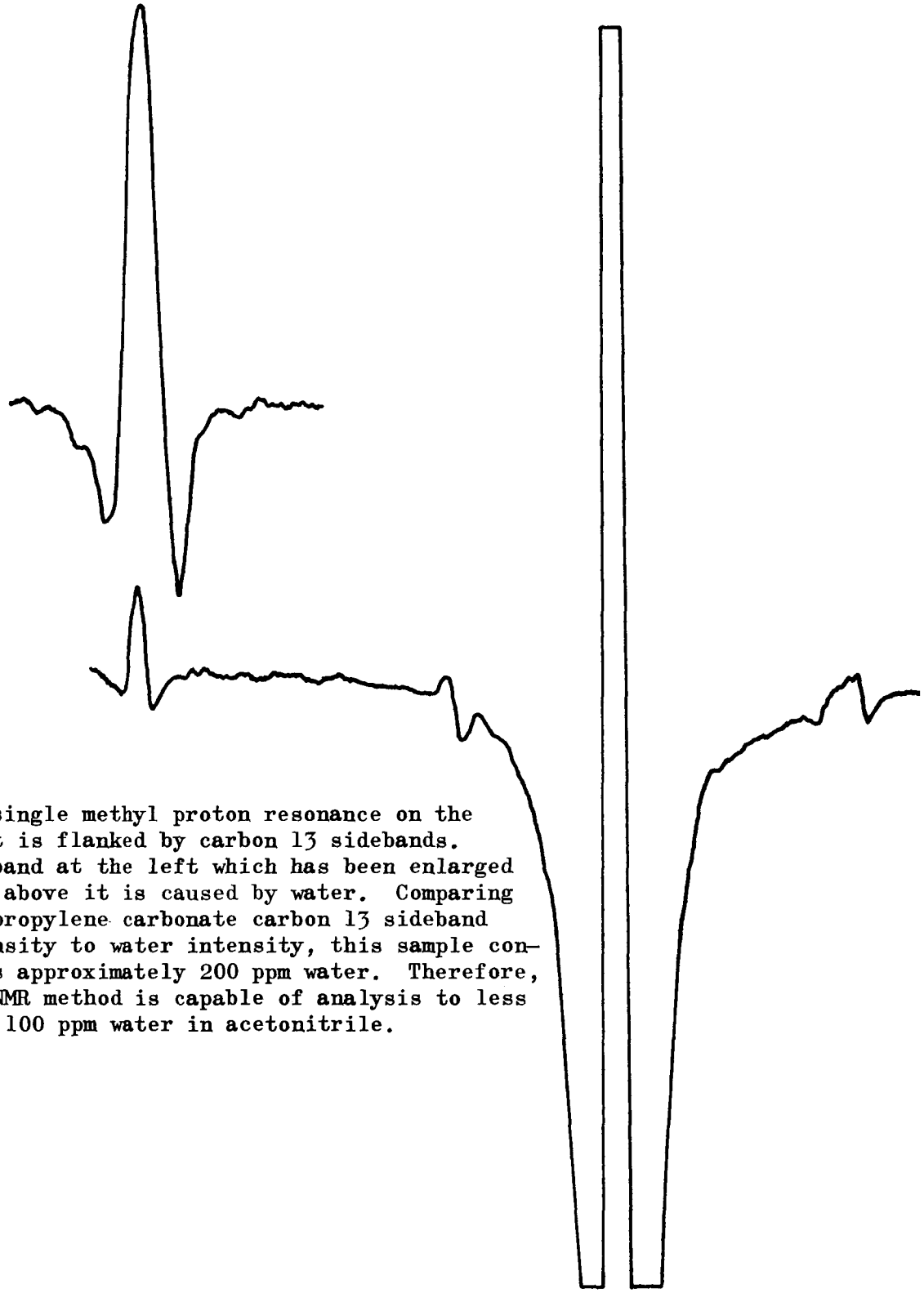
Figure 9 displays the proton spectrum of a sample of acetonitrile which was run to determine whether the water resonance would be separate from the methyl resonance. As it can be seen, there is ample separation of peaks to allow the analysis of water in acetonitrile.

Analysis of Solutes by Spark Source Mass Spectrometry

Five solutes were analyzed by spark source mass spectrometry: lithium chloride (LiCl #2, 99.9 percent, Atomergic Chemetals Division of Gallard Schlesinger), aluminum chloride ($AlCl_3$ #3, 99.999 percent, Rocky Mountain Research, Inc.), lithium fluoride (LiF #2-1, 99.9 percent, Electronic Space Products, Inc.; dried under vacuum at elevated temperature), tetramethylammonium hexafluorophosphate ($TMA.PF_6$ #1, Ozark-Mahoning Company), and anhydrous cupric chloride ($CuCl_2$ #2, reagent grade, Fisher Scientific Co.). These analyses were performed at the Bell & Howell Research Center, Pasadena, California. The results are presented in Table 2 for LiCl, in Table 3 for $AlCl_3$, in Table 4 for LiF, in Table 5 for $TMA.PF_6$, and in Table 6 for $CuCl_2$. Results obtained by emission spectroscopy were added for comparison purposes.

Analyses for tantalum and gold are not presented because tantalum slits were used in the mass spectrometer and the samples were sparked against an ultrahigh purity gold probe. No analysis was made for hydrogen in the cases of LiCl and of $AlCl_3$. Other elements not listed were generally below the limit of 5 or 10 ppm (atomic).

Samples were not prepared under entirely anhydrous conditions. Although the samples were pressed in closed rubber bags, they were trimmed and exposed to the laboratory air during transfer from the inert atmosphere



The single methyl proton resonance on the right is flanked by carbon 13 sidebands. The band at the left which has been enlarged just above it is caused by water. Comparing the propylene carbonate carbon 13 sideband intensity to water intensity, this sample contains approximately 200 ppm water. Therefore, the NMR method is capable of analysis to less than 100 ppm water in acetonitrile.

Figure 9. High Gain Spectrum of Acetonitrile

TABLE 2

IMPURITY CONCENTRATIONS IN LiCl #2 DETERMINED BY SPARK SOURCE MASS SPECTROMETRY AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
Be	0.2	0.42	0.2	<0.3
C	1	120	68	
N	1	6.5	4.3	
O	1	3900	2900	
F	1	17	15	
S	5	8	12	
Na	0.3	180	195	<100
Mg	1	5.4	6.2	2.5
Al	0.5	0.8	1.0	<5
Si	1	2.8	3.8	<10
K	0.5	100	185	<300
Ca	1	6.0	11.5	36
Ti	10	Not detected	(<23)	<4
Cr	1	3.2	7.9	<1
Fe	1	3.3	8.7	<2
Ni	1	13	36	<5
Cu	1	4.4	13	0.6
Zn	1	4.0	12	<100
Ge	10	Not detected	(<34)	<5
Se	1	2.1	7.8	
Br	1	2.0	7.5	
Cd	1	5.3	28	<30
Hg	2	2.1	20	<200

TABLE 3

IMPURITY CONCENTRATIONS IN $AlCl_3$ #3 DETERMINED BY SPARK SOURCE MASS SPECTROMETRY AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy	
	Detection Limit	Content, ppm atomic	Content, ppm per weight	Content (Sample 1), ppm per weight	Content (Sample 2), ppm per weight
Li		Not determined		<50	<50
Be	0.2	1.4	0.4	<0.3	<0.3
B	0.3	0.64	0.21	<30	<30
C	1	91	33		
N	1	58	24		
O	1	2700	1300		
Si				28	54
F	1	24	14		
Na	0.3	57	40	<100	<100
Mg	1	130	95	9.2	12
P	1	51	47		
K	0.5	7.6	8.9	<300	<300
Ca	1	4.9	5.9	9.8	22
Ti	1	(540)	(780)	<4	<4
Cr	1	2.2	3.4	<1	<1
Fe	1	56	94	12	<10
Co	1	20	35	<3	<3
Ni	1	4.4	7.8	<3	<3
Cu	1	8.3	16	21	59
Zn	5	5.8	11.3	<100	<100
Nb	1	6.3	18		
Sb	2	52	190	<40	<40
Hg	2	15	90	<200	<200
Pb				30	<20

TABLE 4

IMPURITY CONCENTRATIONS IN LiF #2-1 DETERMINED BY SPARK SOURCE MASS SPECTROMETRY AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
H	3	290	22	
B	1	2.7	2.3	
C	1	750	690	
N	1	40	43	
O	1	7000	8600	
Na	0.3	4800	8500	<100
Al	0.5	5.8	12.1	4.8
Si	1	28	60	96
P	5	10	24	
S	3	220	540	
Cl	1	1600*	4400*	
K	0.3	270	810	<300
Ca	0.7	14	43	44
V	1	2.0	7.9	<5
Cr	1	2.0	8.0	<1
Cu	1	38*	187*	10
Nb	3	7.0	50	
Sb	5	17	160	<40
Mg				2.2
Pb				16
Fe				4.0
Sn				Trace (<3)
Ni				4.4

*May be caused by cross sparking of a copper chloride sample also in the the mass spectrometer.

TABLE 5

IMPURITY CONCENTRATIONS IN TMA.PF_6 #1
DETERMINED BY SPARK SOURCE MASS SPECTROMETRY
AND EMISSION SPECTROSCOPY

	Spark Source Mass Spectrometry			Emission Spectroscopy
Impurity	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
Li	1	27	20	
B	3	5.7	6.8	<30
O	3	290	510	
Na	1	8.3	20.9	<100
S	20	Not detected	<70	
Cl	3	960*	3720*	
K	1	2.3	9.9	<300
Cu	3	2400*	16700*	5.2
Zn	5	27	194	<100
Mg				8
Si				50
Fe				Trace(<30)
Ca				25

*May be caused by residuals in the mass spectrometer

TABLE 6

IMPURITY CONCENTRATIONS IN $CuCl_2$ #2
DETERMINED BY SPARK SOURCE MASS SPECTROMETRY
AND EMISSION SPECTROSCOPY

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
H	3	36	0.8	
Li	0.3	1200*	190*	< 200
C	1	20	5	
N	1	15	5	
O	1	480	170	
F	1	16	7	
Na	0.3	79	41	
Mg	0.7	1.1	0.6	4.1
Al	0.5	2.9	1.7	
Si	5	Not detected	< 3	4.1
Ca				8.0
P	1	1.7	1.2	
S	5	27	19	
K	0.3	31	27	
Ca	0.7	2.9	2.6	
Ti	1	3.8	4.1	
V	1	13	15	
Cr	1	7.5	8.7	6.9
Mn	1	3.7	4.5	
Fe	1	100	125	34
Ni	1	46	60	Trace <10

*May be due to residuals in the mass spectrometer.

TABLE 6
(Continued)

Impurity	Spark Source Mass Spectrometry			Emission Spectroscopy
	Detection Limit, ppm atomic	Content, ppm atomic	Content, ppm per weight	Content, ppm per weight
Zn	3	6.1	8.9	
Ga	0.7	6.7	10.4	
As	1	9.7	16.2	
Se	2	5.4	9.5	
Br	1	11	20	
Ag	< 5			11
Y	0.7	1.4	2.8	
Ru	2	9.7	22	
Cd	3	50	125	<100
Sn	4	5.2	13.8	
Sb	3	4.4	12.0	
Pb	3	5.2	24.1	26

box to the spark chamber. The trimmed faces changed appearance. The oxygen content represented, therefore, an upper limit for the true oxygen content of the analyzed products which is probably much lower.

Memory effects caused by previously analyzed materials and cross-sparking of other samples in the mass spectrometer evidently interfered in several instances. The analysis of lithium in $AlCl_3$ is not presented because a high value for lithium was obtained; this resulted from the preceding sparking of the LiCl sample. The analyses for chlorine in LiF and TMA.PF_6, copper in LiF and TMA.PF_6, and for lithium in $CuCl_2$ and TMA.PF_6 are also uncertain for the same reason.

Two exposures on the mass spectrometric photographic plate indicated a very high titanium content of the $AlCl_3$, but a corresponding amount of titanium could not be detected on the several other exposures. This phenomenon has not been explained, but a possibility would be a heterogeneity in the sample being sparked. An analysis of an electrolyte containing the $AlCl_3$ may be made at a later date using atomic absorption spectroscopy. This will determine whether the overall titanium content is negligible, as assumed.

Analysis of Solutes by Emission Spectroscopy

The results obtained by emission spectroscopy are listed in Table 7. The analyses were performed by the Pacific Spectrochemical Laboratory, Inc., Los Angeles, California. The results are considered semiquantitative, with an accuracy of ±50 percent and a reproducibility of ±15 percent. Empirical corrections were made based on the major anion present, because individual calibrations for most of the matrices were not available. Impurities not listed were below the detection limits which were reported previously for a lithium carbonate matrix (Ref. 1).

TABLE 7

EMISSION SPECTROSCOPIC ANALYSIS RESULTS FOR SOLUTES

(Impurity Levels in ppm per Weight)

Solute / Impurity	$LiClO_4$ #2	LiCl #2	LiF #2	LiF #3	TMA·PF_6 #1	Morph·PF_6 #1	$AlCl_3$ #3	$AlCl_3$ #3	CuF_2 #2	$CuCl_2$ #1	$CuCl_2$ #2
B						16					
Mg	3	3	2	1	8	8	9	12	35	6	4
Al			5	17					170		
Si	10		96	12	50		28	54	Trace (<4)	7	4
Ca	17	36	44	34	25	49	10	22	86	5	8
Cr									5		7
Mn									23		
Fe	2		4	13	Trace (<30)		12	Trace (<10)	1100	11	34
Ni			4						970	Trace (<10)	Trace (<10)
Cu	4	1	10	15	5	6	21	59			
Sr						Trace (<3)					
Ag									6	2	11
Sn	4						Trace (<20)		400		
Sb						240					
Pb	16		16	20			30		120		26

Discussion of Solute Analysis Results

After considering the results obtained by spark source mass spectrometry and emission spectroscopy, the following conclusions were reached.

The results obtained by both methods reveal fair agreement. There are some discrepancies beyond typical claims of accuracy (e.g., 20 percent for spark source mass spectrometry, 50 percent for emission spectroscopy); mass spectrometric analysis generally indicated somewhat higher impurity contents. However, some deviations were also found in the results obtained with two samples of the same $AlCl_3$ stock (Tables 3 and 7) with the established emission spectroscopic method for which a reproducibility of 15 percent is being claimed.

Although these discrepancies exist, the compounds analyzed contained only few impurities at a level of 100 ppm or higher.

In LiCl, impurities such as sodium (195 ppm) and potassium (185 ppm) should not interfere significantly or affect the data to be obtained. The oxygen content indicated is probably caused by contamination of the sample by atmospheric moisture. This chemical will be used for electrolyte solutions after drying under vacuum at elevated temperatures.

In $AlCl_3$, the magnesium, iron, antimony and mercury contents were approximately 100 ppm according to spark source spectrometry, but the emission spectroscopy indicated lower values. The determination of the titanium content is ambiguous. Again, the oxygen content may be caused by handling of the sample.

Of the five chemicals analyzed by both methods, the LiF sample revealed the largest amount of impurities. The oxygen content may be high because of sample handling, but the oxygen appears to be present in a form other

than water, because only a low hydrogen content was found. The sodium content as determined by mass spectrometry, was 8500 ppm, but below 100 ppm as determined by emission spectroscopy; an additional flame photometric test of a solution is advisable. Results for copper and chlorine are ambiguous; emission spectroscopy indicated a low copper content, and an analysis for chlorine may be necessary using conventional analytical techniques. Sulfur and carbon contents indicate the presence of possibly sulfate and carbonate. Because lithium fluoride has a low solubility in the solvents and electrolytes under consideration, only small quantities of this material will be used, and therefore only small quantities of impurities will be introduced into the solutions. LiF will be used without further purification. However, in solubility determinations, an analysis based on fluorine contents rather than lithium contents seems advisable.

Tetramethylammonium hexafluorophosphate contains only negligible amounts of impurities. Organic impurities have not been determined specifically.

In $CuCl_2$, many impurities were discovered, but all at low levels. Only iron and cadmium were found at impurity levels of approximately 100 ppm. It is assumed that the high lithium value was caused by the residuals in the mass spectrometer and the oxygen content was caused by handling.

It is recommended that all of the five chemicals tested be used as received from the supplier. Drying under vacuum at elevated temperatures is advisable for LiCl and LiF.

PHYSICAL PROPERTY DETERMINATIONS

Density Measurements

Density measurements were made both on pure DMF and on LiCl/DMF solutions at 25 C using a standard Weld pycnometer. The dry pycnometer was weighed, transferred to the dry box, and filled with the solution of interest. The pycnometer was then transferred to the constant temperature bath and allowed to equilibrate. The capillary plug was inserted, and the pycnometer was again weighed. The weight of solution was corrected to weight in vacuum. A similar procedure with distilled water allowed the determination of the volume of the pycnometer.

The density measurements are presented in Table 8. The density of 0.9436 gm/cm^3 for pure DMF compares favorably with the value of 0.9439 found by Prue and Sherrington (Ref. 4) and of 0.9442 gm/cm^3 found by Leader and Gormley (Ref. 5). Graphic interpolation furnished the density values used for the viscosity measurements presented in the following paragraph.

TABLE 8

DENSITIES OF SOLUTION OF LiCl in DMF at 25 C

Concentration, molarity	Density, gm/ml
0	0.9436
0.3066	0.9569
1.0221	0.9840
2.24 (Saturated Solution)	1.0235

Viscosity Measurements

Viscosities of DMF and of LiCl/DMF solutions were measured using a Cannon-Fenske Routine Viscometer (size 25). The viscometer was thoroughly cleaned with cleaning solution, washed with conductivity water and acetone, and dried in a stream of dry air. The viscometer was transferred to the dry box and 5 cc of solution was added with a pipette. The viscometer was then placed in the constant temperature bath, allowed to equilibrate, and measurements were taken using an electrical timer. A similar procedure with distilled water allowed the viscosity to be calculated from the equation:

$$\frac{\eta}{\eta_0} = \frac{dT}{d_0 T_0}$$

where

η = viscosity of the solution

d = measured density of the solution

T = time of efflux of solution

η_0 = known viscosity of distilled water

d_0 = known density of distilled water

T_0 = time of efflux of distilled water

The similarity of efflux times renders the kinetic energy correction negligible except perhaps for the 1.022 M solution.

The viscosities determined by the preceding procedure at 25 C are shown in Table 9. The value 7.93×10^{-3} poise for pure DMF is in good agreement with the value of 7.96×10^{-3} poise obtained by Prue and Sherrington (Ref. 4) and by Ames and Sears (Ref. 6).

TABLE 9

VISCOSITIES OF SOLUTIONS OF LiCl in DMF at 25 C

LiCl-Concentration, mole/liter	Density, gm/ml	Efflux Time, seconds	Viscosity, millipoises
Distilled H_2O	0.997	434.7	8.95
0.000	0.944	407.0	7.93
8.177×10^{-3}	0.944	409.9	7.99
4.088×10^{-2}	0.945	420.4	8.20
2.044×10^{-1}	0.952	473.5	9.31
3.066×10^{-1}	0.957	509.4	10.07
1.022	0.984	893.2	18.15

Solubility Measurements

The solubility of LiCl in DMF was determined at 25 and 60 C respectively. The results are presented in Table 10. Saturated solutions were prepared in volumetric flasks by adding an excess of LiCl, heating to 80 C for approximately 2 hours, and allowing the flask to equilibrate in the constant temperature baths overnight.

TABLE 10

SOLUBILITIES OF LiCl in DMF at 25 C

Temperature, C	Solubility, molar	Solubility (Average), molar
60	3.75	
	3.76	3.76
25	2.45	
	2.40	2.42
	2.40	

The solubility of LiCl at 60 C was measured by drawing approximately 5 cc of saturated solution into a weighed glass syringe. The syringe was again weighed and the contents were washed into a 100-milliliter volumetric flask with conductivity water. The flask was filled to the 100-milliliter level and a 10-milliliter sample was titrated with 0.1984 M $AgNO_3$ using dichlorofluorescein as the indicator. Duplicate determinations were made.

Three determinations of the solubility of LiCl at 25 C were made. The first determination was made using the same procedure as for the 60 C measurements, while the following two determinations involved taking 5 cc samples, diluting to 100 cc with conductivity water, and titrating as done previously.

The molar solubility of $AlCl_3$ in DMF was measured at 25 and 60 C by taking 5 cc samples of the saturated solutions, diluting with conductivity water, and titrating with standard $AgNO_3$ solution. The results are presented in Table 11.

TABLE 11

SOLUBILITY OF $AlCl_3$ in DMF at 25 C

Temperature, C	Solubility, molar
60	0.273
25	0.0773

Conductance Measurements

Conductivity values of solutions were determined in Freas cells as described previously (Ref. 1). Conductance values obtained with LiCl/DMF solutions are presented in Table 12. The relationship between the equivalent conductance and the square root of the concentration is presented in Fig. 10 for the temperatures of 25 and 60 C. The results are also shown on an expanded scale in Fig. 11.

No irregularities were observed, except at the elevated temperature of 60 C. There, the conductance value of the pure solvent and of the solution at the lowest solute concentration were somewhat unstable. This introduced an uncertainty in the conductance data and particularly in the solvent correction.

Equivalent conductance values at infinite dilution of Λ_o = 84.0 $ohm^{-1}equ^{-1}cm^2$ at 25 C and of Λ_o = 118 $ohm^{-1}equ^{-1}cm^2$ at 60 C were obtained. The 25 C value compares with Λ_o = 81.4 $ohm^{-1}equ^{-1}cm^2$ found previously at Rocketdyne (Ref. 1) in an electrolyte containing lower quality solvent and solute and a literature value of 80.2 $ohm^{-1}equ^{-1}cm^2$ (Ref. 4).

TABLE 12

SPECIFIC CONDUCTANCE (λ) AND EQUIVALENT CONDUCTANCE (Λ)
OF LiCl/DMF AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$, molar$^{1/2}$	λ (25 C), ohm^{-1} cm^{-1}	Λ^* (25 C), ohm^{-1} equ^{-1} cm^2	λ (60 C), ohm^{-1} cm^{-1}	Λ^* (60 C), ohm^{-1} equ^{-1} cm^2
1.022	1.011	8.50×10^{-3}	8.32	1.115×10^{2}	10.91
0.204	0.452	4.78×10^{-3}	23.36	5.87×10^{-3}	28.71
0.0409	0.202	1.69×10^{-3}	41.34	2.13×10^{-3}	52.15
0.00818	0.0904	4.89×10^{-4}	59.70	6.47×10^{-4}	78.86
0.001635	0.0404	1.21×10^{-4}	73.21	1.66×10^{-4}	100.3
0.000327	0.0181	2.73×10^{-5}	80.61	3.83×10^{-5}	111.1
0.0000654	0.00809	6.38×10^{-6}	82.72	8.32×10^{-6}	97.1
0		9.7×10^{-7}		2.0×10^{-6}	
			Extrapolated: $\Lambda_o = 84.0$		Extrapolated: $\Lambda_o = 118$

Λ^*: Equivalent conductance, corrected for conductance of pure solvent

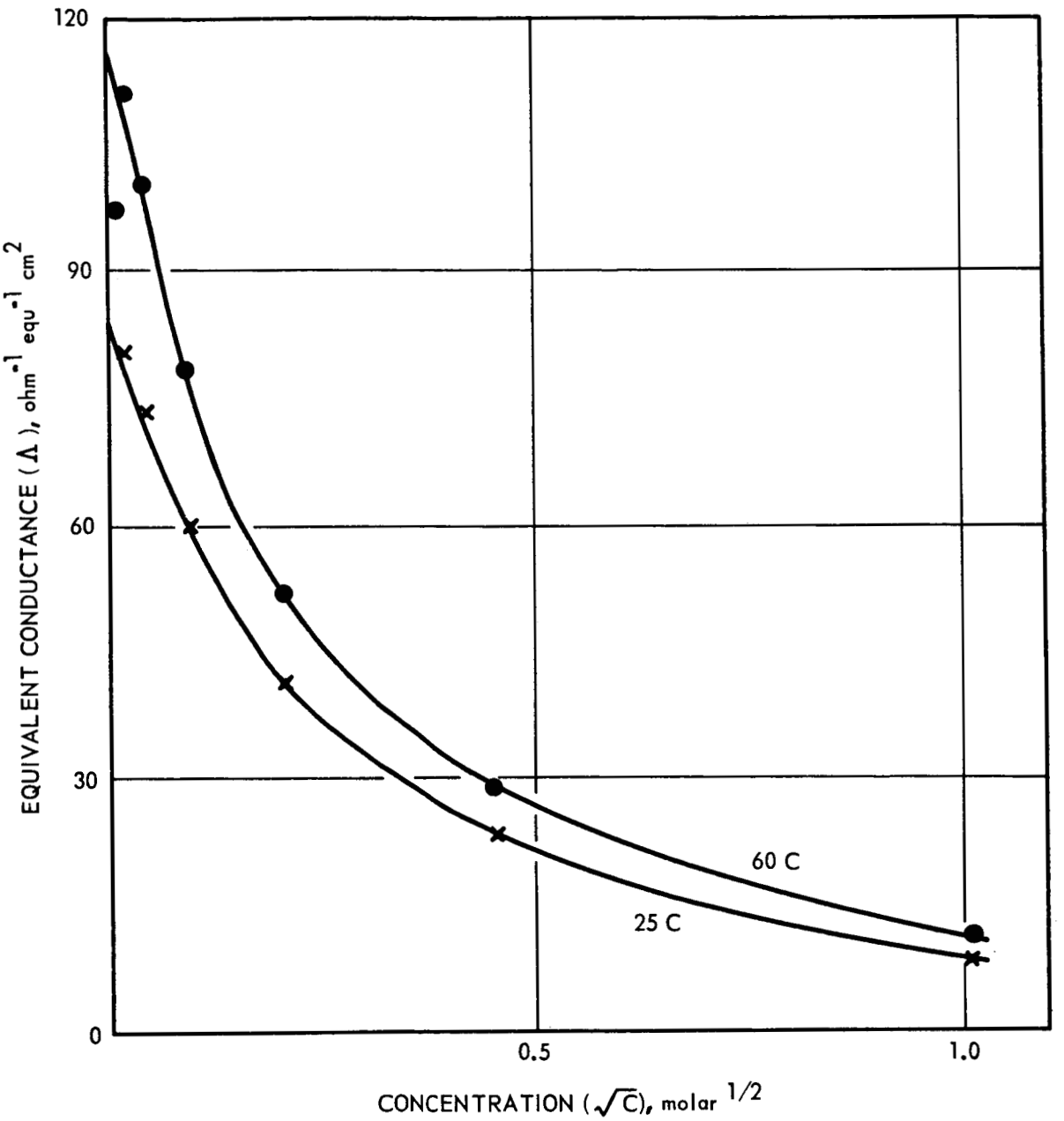


Figure 10. Equivalent Conductance of LiCl in DMF at 25 and 60 C

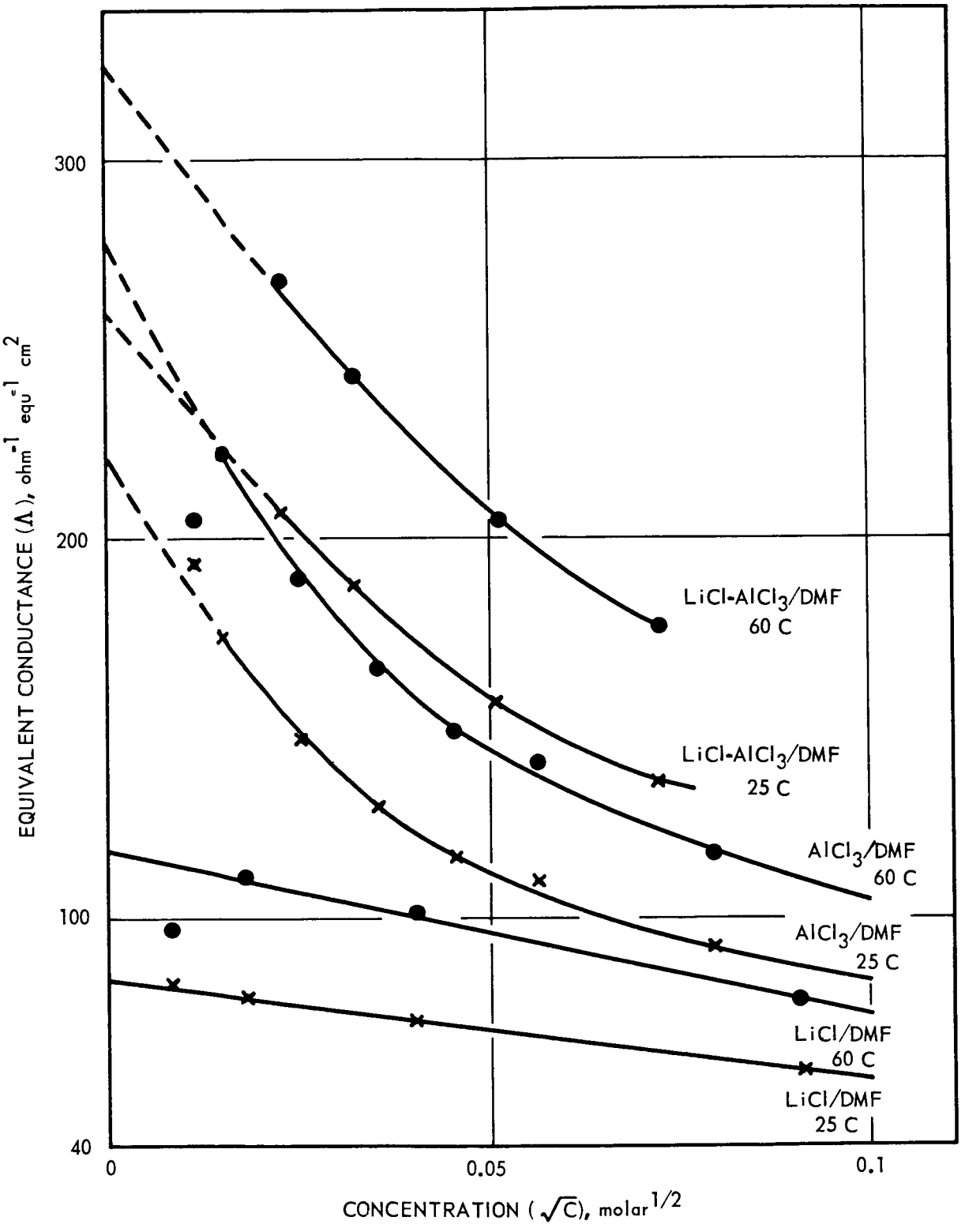


Figure 11. Equivalent Conductance of LiCl/DMF, $AlCl_3$/DMF, and LiCl-$AlCl_3$/DMF at 25 and 60 C

Conductance values obtained with $AlCl_3$/DMF solutions are presented in Table 13. Because of the limited solubility of $AlCl_3$ in DMF, no measurements could be taken at higher concentrations. The graphic extrapolation to zero concentration is shown in Fig. 11; it yielded values of Λ_o = 220 $ohm^{-1}equ^{-1}cm^2$ at 25 C and Λ_o = $280^{-1}equ^{-1}cm^2$ at 60 C. This extrapolation is somewhat uncertain because a straight line was not obtained.

Results obtained with equimolar solutions of LiCl and $AlCl_3$ in DMF are presented in Table 14 and are also represented in Fig. 11. Concentration values refer to each component, i.e., a 0.05 molar LiCl-$AlCl_3$ solution contains 0.05 mole of LiCl and 0.05 mole of $AlCl_3$ per liter. Extrapolation resulted in Λ_o = 260 $ohm^{-1}equ^{-1}cm^2$ for 25 C and Λ_o = 325 $ohm^{-1}equ^{-1}cm^2$ for 60 C.

A comprehensive analysis of the data has not yet been conducted but the following has been determined:

1. The equivalent conductance of LiCl at infinite dilution is smaller in DMF than in water.
2. Incomplete dissociation is indicated by negative deviations from the limiting law according to Onsager.
3. The extrapolation in the case of $AlCl_3$ containing electrolytes is uncertain, because the relationship is not linear and data points have greater relative experimental errors at lower concentrations.
4. $AlCl_3$/DMF electrolytes contain a greater number of conductive species than LiCl/DMF. $AlCl_3$ possibly dissociates largely into Al^{+++} and $3Cl^-$ at infinite dilution.
5. The sum of the Λ_o values for LiCl/DMF and $AlCl_3$/DMF electrolytes does not equal the Λ_o value found for the LiCl-$AlCl_3$/DMF mixed electrolyte.

TABLE 13

SPECIFIC CONDUCTANCE (λ) AND EQUIVALENT CONDUCTANCE (Λ) OF $AlCl_3$/DMF AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$, molar$^{1/2}$	λ (25 C), ohm^{-1} cm^{-1}	Λ^* (25 C), ohm^{-1} equ^{-1} cm^2	λ (60 C), ohm^{-1} cm^{-1}	Λ^* (60 C), ohm^{-1} equ^{-1} cm^2
0.0638	0.259	3.18×10^{-3}	49.8	4.24×10^{-3}	66.4
0.00638	0.0798	5.83×10^{-4}	91.4	7.52×10^{-4}	117.9
0.00319	0.0565	3.51×10^{-4}	110.1	4.51×10^{-4}	141.4
0.002125	0.0461	2.47×10^{-4}	116.2	3.18×10^{-4}	149.4
0.001275	0.0357	1.65×10^{-4}	129.3	2.13×10^{-4}	166.6
0.000638	0.0253	9.44×10^{-5}	147.5	1.21×10^{-4}	189.2
0.000255	0.0150	4.50×10^{-5}	174.9	5.74×10^{-5}	222.7
0.0001275	0.0113	2.51×10^{-5}	193:7	3.18×10^{-6}	204.7
0	0	3.5×10^{-7}	Extrapolated: $\Lambda_o = 220$	5.66×10^{-7}	Extrapolated: $\Lambda_o = 280$

TABLE 14

SPECIFIC CONDUCTANCE (λ) AND EQUIVALENT CONDUCTANCE (Λ) OF $LiCl-AlCl_3$/DMF AT 25 AND 60 C

Concentration (C), molar	$\sqrt{C}$ molar$^{1/2}$	λ (25 C), ohm^{-1}cm^{-1}	Λ* (25 C), ohm^{-1}equ^{-1}cm^{2}	λ (60 C), ohm^{-1}cm^{-1}	Λ* (60 C), ohm^{-1}equ^{-1}cm^{2}
0.0528	0.230	3.79×10^{-3}	71.84	4.95×10^{-3}	93.7
0.00527	0.0726	7.19×10^{-4}	136.2	9.34×10^{-4}	176.6
0.00264	0.0514	4.15×10^{-4}	157.2	5.42×10^{-4}	204.9
0.001055	0.0325	1.985×10^{-4}	187.4	2.60×10^{-4}	243.9
0.00528	0.0230	1.096×10^{-4}	206.3	1.436×10^{-4}	268.1
0		8.3×10^{-7}	Extrapolated: $\Lambda_o = 260$	2.2×10^{-6}	Extrapolated $\Lambda_o = 325$

Measurement of Transference Numbers by the Hittorf Method

A Hittorf cell was fabricated for measurements of transference numbers. The cell design of Wall, Stent, and Ondrejcin (Ref. 7) was modified to allow easy immersion of part of the cell into the constant temperature bath. The high electrolyte resistances may cause excessive cell heating and require that the cell be cooled. The cell is presently being tested with an aqueous electrolyte.

WORK PLANNED FOR NEXT QUARTER

PREPARATION OF ELECTROLYTES

The distillation of solvents will continue. A complete vapor phase chromatographic characterization of acetonitrile will be made.

The purity of the distilled products will be checked on a routine basis by a chromatogram with a Porapak Q column for propylene carbonate and dimethyl formamide and by Karl Fischer titration for acetonitrile.

Analysis of solutes will be continued.

PHYSICAL PROPERTY DETERMINATIONS

Determinations of physical properties will continue using solute-solvent combinations which have been sufficiently characterized and purified. Nuclear magnetic resonance studies will be made using LiCl and $AlCl_3$ as solutes, and dimethyl formamide and propylene carbonate as solvents.

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A complete vapor phase chromatographic analysis of dimethyl formamide was conducted, and several techniques were utilized to verify the water content of propylene carbonate and dimethyl formamide. Solutes were characterized by spark source mass spectrometry and emission spectroscopy. Physical properties such as the density, viscosity, and conductance of electrolytes containing LiCl and/or $AlCl_3$ in dimethyl formamide were determined.

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